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DEVELOPMENT OF ANALYTICAL METHODS FOR MONITORING THERMAL EOR PRODUCING WELLS

Technical Report for the Period May 15, 1989 - April 30, 1990

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DEVELOPMENT OF ANALYTICAL METHODS

FOR MONITORING THERMAL EOR PRODUCING WELLS

Technical Report for the Period
May 15, 1989-April 30, 1990

Prepared by

Béla Verkoczy

and

Meseret Jimale

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MICROMEDIA

SUMMARY

1. A reproducible high performance liquid chromatographic (HPLC) method for separating saturates, aromatics, resins and asphaltenes (SARA) fractions of crude oil has been adapted and improved over the technical literature method (Table 3).

2. The gravimetric quantification of the HPLC separated fractions has been improved. A very good material balance of the SARA fractions was obtained for the heavy oils (API gravity <15°), and a reasonably good material balance for lighter oils (API gravity >15°) (Table 5).

3. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy was introduced to investigate the oil and its SARA constituents as a complementary technique (Tables 7, 8, 9 and A13). This technique was successfully used to demonstrate variations in enhanced oil recovery (EOR) produced oil composition as a function of time.

4. The HPLC technique was compared to the existing techniques according to reinjection and ultraviolet (UV) detection (Syncrude). NMR analysis of fractions showed that a clean separation was achieved (Tables A10 and A11): <1% cross-contamination of aromatics in saturates vs. 5-12% cross-contamination of similar fractions in the Syncrude technique.

5. The time and amount of solvent required for SARA determination using the HPLC technique were far less than the other techniques (50 min and 450 mL vs. 2 days and 2 L).

6. Heavy oils from four wells, when analyzed by the HPLC SARA method, showed some regional variation in oil composition. A more detailed analysis of these SARA fractions by the proton and carbon-13 NMR indicated that variations were greatest in the aromatic, then the resin and asphaltene fractions.

7. Significant variations were observed in the SARA composition of oils collected from the same well at different times. These differences are real and not caused by the variations in reproducibility of the analytical techniques used. It is concluded that the changes in the ratios of aliphatic to aromatic protons and in the ratios of aliphatic to aromatic carbon-13 may be assigned to several effects. Essentially dilution may occur by distillation and cracking leading to a higher proton aliphatic to proton aromatic ratio. A condensation effect (coking) may be inferred from a lowered aliphatic to aromatic carbon ratio.

8. The most convincing evidence for fireflood effects was offered by the GC/MS data of the produced oils. Compounds were identified that could be found only in the affected well samples. Toluene was found in all the wells in varying concentrations, but none in the primary well sample. When developed, this method would be a very useful as a monitoring device and for further analysis of SARA fractions.

SOMMAIRE

1. Nous avons adapté une méthode reproductible par chromatographie de liquide à haute performance (HPLC) pour séparer les fractions saturés, aromatiques, résines, asphaltènes (SARA) du pétrole brut et l'avons améliorée par rapport à la méthode que l'on trouve couramment dans les divers articles et journaux sur le sujet (tableau 3).

2. Nous avons amélioré la quantification gravimétrique des fractions séparées par la méthode HPLC. Nous avons obtenu un très bon bilan matière des fractions SARA pour les pétroles lourds, et un bilan matière raisonnablement bon pour les pétroles plus léger (tableau 5).

3. Nous avons utilisé une technique de spectroscopie à résonance magnétique nucléaire au ^{1}H et ^{13}C (RMN) pour procéder à une étude plus poussée du pétrole et de ses composantes SARA (tableaux 7, 8, 9 et A13). Cette méthode a été utilisée avec succès pour démontrer les variations dans la composition du pétrole produit par récupération assistée (EOR) en fonction du temps.

4. Nous avons comparé la technique HPLC aux techniques existantes selon la détection par réinjection et ultraviolets (UV) (technique Syncrude). L'analyse RMN des fractions a montré que l'on obtenait une séparation nette (tableaux A10 et A11): «1% de contamination croisée des aromatiques avec les saturés contre 5-12% de contamination croisée des fractions similaires avec la technique Syncrude.

5. Le temps nécessaire et la quantité de solvant nécessaire pour déterminer les fractions SARA à l'aide de la technique HPLC étaient bien moindres qu'avec les autres techniques (50 min et 450 mL contre 2 jours et 2 L).

6. Des pétroles lourds provenant de quatre puits on montré certaines variations régionales de composition, après analyse avec la méthode SARA HPLC. Une analyse plus détaillée de ces fractions SARA par spectroscopie NMR au proton et au carbone-13 a indiqué que les variations étaient les plus importantes dans les fractions aromatiques, puis dans l'ordre dans les résines et les asphaltènes.

7. Nous avons noté des variations significatives dans la composition SARA des pétroles extraits d'un même puits à des moments différents. Ces différences sont réelles et non pas causées par les variations de reproductibilité des techniques d'analyse utilisées. Nous en avons conclu que les changements dans les rapports entre protons aliphatiques et aromatiques et carbone-13 aliphatique et aromatique peuvent être attribués à plusieurs causes. Essentiellement, la dilution peut être causée par distillation et craquage entraînant un rapport plus élevé de protons aliphatiques par rapport aux protons aromatiques. On peut déduire un effet de condensation (coking) d'un rapport réduit de carbone aliphatique par rapport au carbone aromatique.

8. La preuve la plus concluante des effets de l'injection a été fournie par les données GC/MS relatives aux pétroles produits. Des composés on été identifiés qui ne pouvaient se trouver que dans les échantillons affectés. Nous avons découvert du toluène dans tous les puits, à diverses concentrations, mais n'en avons pas trouvé dans l'échantillon primaire. Lorsque'elle aura été développée, cette méthode constituera un moyen très utile de contrôle et d'analyse plus poussée des fractions SARA.

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PROJECT TEAM

B. Verkoczy	:	Project Leader
M. Jimale	:	Research Scientist

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I. INTRODUCTION

This project is aimed at the development of analytical methods for monitoring thermal enhanced oil recovery (EOR) producing wells. Background information, the objectives of the investigation, and a summary of the previous work are given in the following subsections.

Background

The petroleum industry's need for more detailed and accurate chemical composition data of produced oil has significantly increased in recent years because of changing exploration, production and refining environments. A significant regional variation in the composition of the heavy oil obtained from different Saskatchewan reservoirs is expected in terms of saturates, aromatics, resins and asphaltenes. Numerous methods for the chemical component types of the separation of oil have been reported in the literature. The Syncrude analytical technique[1] is one of the methods widely accepted by the petroleum industry. It is used to compare the results with other methods. Our experience indicated that it is not a reproducible method, and one that requires a considerable amount of time and large volumes of solvents for SARA determination. This method also shows large cross-contaminations in the saturate and aromatic fractions. As a result, exploratory work was carried out at Saskatchewan Research Council (SRC) Petroleum Research to develop a SARA method that was a HPLC technique, time-saving, reproducible, and field application oriented.

Project Objectives

1. Develop a reproducible high performance liquid chromatographic (HPLC) method for separating saturate, aromatic, resin and asphaltene (SARA) fractions of crude oil.

2. Improve the gravimetric quantification of the separated fractions.

3. Introduce ^{1}H and ^{13}C-NMR spectroscopy for investigating the oil and its SARA constituents either as an independent or a complementary technique.

4. Compare the existing and new techniques for selecting the correct method(s) for the quantitative determination of SARA constituents in crude oil.

5. Reduce overall time and solvent used for SARA determinations.

6. Demonstrate the regional variation of heavy oil composition (inter-reservoir comparison).

7. Demonstrate the variations in SARA composition of oils produced from the same reservoir under thermal EOR as a function of time.

8. Look for new products in fireflood produced oils by using GC-MS. Relate them to operating parameters if available.

Summary of Previous Work

A semiquantitative method to determine saturate, aromatic, resin and asphaltene (SARA) fractions was developed for comparative studies and for monitoring changes in oil composition for a given well.

- Preliminary removal of asphaltenes from oil samples to prevent irreversible adsorption of these polar groups onto the column packing.

- A number of analytical columns were tested for their ability to resolve fractions.

- Modification of the Grizzle and Sablotny[1] solvent delivery program to maximize separation and recovery of fractions.

- Recovery and separation of maltenes.

- Adapted the method to direct microfiltration and injection of oil samples.

2. EXPERIMENTAL

2.1 Oil Sample Origin and Preparation

Twelve oil samples, from Murphy's Eyehill reservoir, were collected in sets of four at three different periods, May 1987, January 1989 and June 1989. These oils are listed in Table 1. To clean the crude oil, water was removed before the HPLC or GC-MS methods were used. For the SARA separation technique, oil cleanup was performed using 250 ppm de-emulsifying agent. For GC-MS analysis, calcium chloride was used. The composition of the de-emulsifying agent had not been specifically given. It was reported that it contains considerable amounts of methanol or propanol, 30-40% reactive ingredient, and the rest contains aromatic oil with a very high boiling point.

Table 1. Sample Origin and Description

Sample No.	Well Location (Eyehill)	Date of Sampling
1-21	1-21-40-28 W3M	May 1987
9-16	9-16-40-28 W3M	May 1987
16-16	16-16-40-28 W3M	May 1987
D16-16	D16-16-40-28 W3M	May 1987
1-21	1-21-40-28 W3M	January 1989
9-16	9-16-40-28 W3M	January 1989
16-16	16-16-40-28 W3M	January 1989
D16-16	D16-16-40-28 W3M	January 1989
1-21	1-21-40-28 W3M	June 1989
9-16	9-16-40-28 W3M	June 1989
16-16	16-16-40-28 W3M	June 1989
D16-16	D16-16-40-28 W3M	June 1989

The cleanup procedure for both analytical techniques is as follows: to each of the oil samples, the demulsifying agent (or $CaCl_2$) was added,

stirred and left in the oven (70°C) for one hour. The sample was then shaken and again placed in the oven at the same temperature overnight. The next day the water that had settled at the bottom was removed using a syringe. The oil was transferred to a plastic container and centrifuged for two hours (temperature 35°C, 10^4 rpm). The oil sample was then checked under a microscope for water content (approximately <0.5% of water is acceptable).

2.2 Separation of Oil into Maltene and Asphaltene Fractions

The crude oil sample weight of 3.75 g was diluted to 150 mL using HPLC grade pentane in a 200-mL brown bottle with a sealed teflon-lined cap. After shaking the solution 5-10 min to dissolve the maltenes, it was left on a bench for at least two hours. The solution was shaken again to avoid any deposition of asphaltenes at the bottom of the container, and filtered. The filter paper used for the separation of asphaltenes from maltenes was membrane filter 100 N, type SM 11106, diameter of 47 mm and pore size 0.45 μm. The asphaltenes collected were transferred to a pre-weighed aluminum dish and filter paper. They were left on the bench to dry for two hours and weighed.

The filtered maltene was volumetrically transferred to a 50-mL round-bottomed flask. Two techniques were used in maltene fraction preparation. In the first method, the maltene solution was rotor-evaporated for 5 to 7 min at 70°C, transferred volumetrically to a pre-weighed 50-mL round-bottomed flask, and rotor evaporated for 5 min using a high vacuum pump. The maltenes were then weighed by difference. A known weight of maltenes was diluted in hexane to make a concentration range of 60 to 65 mg/mL. In the second method, the maltene solution was rotor-evaporated concentrated for 3 to 4 min at 70°C, and for 2-3 min at 70°C and 640 mm Hg vacuum still containing some solvent. Then the weight of the maltene was determined by weight difference of the crude oil and asphaltenes. The whole maltene was then diluted to 50 mL using hexane. This made approximately 60 to 65 mg/mL concentration.

2.3 Separation of Maltene in Saturate, Aromatic and Resin (SAR) Fractions Using Different Methods

A. High Performance Liquid Chromatography (HPLC) System

Instrumentation

For HPLC separation, a Perkin-Elmer Series 4 liquid chromatograph solvent delivery system was used (LC). The Perkin-Elmer LC1-100 Laboratory computing integrator was connected with the LC terminal. This was interconnected with two detectors (Perkin-Elmer LC-25 Refractive Index and LC-85B variable wavelength uv, visible spectrophotometer). The Perkin-Elmer ASV-1 automatic switching valve was connected with the system. The injectors and switching valves were of Rheodyne-type. Model 202 fraction collector with a fraction controller 201-202 was attached with the system. The integration, solvent delivery program, and collection of the fractions would begin at the same time right after the sample was injected and the "run" button pressed. The injection loop used in the experiment was a 1-mL loop. A constant wavelength of 254 nm was used in the uv-spectrophotometer.

Choice of Column

In SAR separation, two semipreparative sized Alltech Econosil Amino-Bonded silica columns (cat. no. 6237) were used in tandem. The length of the column was 25 cm, with 10 mm internal diameter and 10 µm particles. The life-time of the column reported by Grizzle and Sablotny[1] was more than 500 sample separations with the loading of 30-65 mg maltene samples. The theoretical plates for 10 µm columns are 25 000 plates per meter.

Solvent Delivery Program

All solvents used for SAR separation are HPLC grade. The solvents include hexane and methylene chloride for separation, methylene chloride and isopropanol for regeneration of the column at the end of the day after a

series of runs, and a reactivation agent for regenerating the column once every two to three weeks. The composition of the reactivation agent released by the manufacturers is said to contain 98% hexane and 2% unknown solvent. We believe it might also contain methanol and glacial acetic acid as the active ingredient. All of the solvents, with the exception of the reactivation agent, were received from Caledon Laboratories Ltd. The reactivation agent was received from Mandel Scientific Company Ltd.

The original solvent delivery method, developed by Grizzle and Sablotny,[1] and the modified version used for SAR separation[2] are listed in Tables 2 and 3, respectively. Regeneration of the column, using methylene chloride and isopropanol in a flow rate of 3-4 mL/min for 30 min for each, was performed in the backflush mode at the end of the day after a series of runs. The following day, before the first injection, methylene chloride was run in the backflush mode with a flowrate of 4 mL/min for about 30 min followed by hexane at 4 mL/min for another 30 min in the same mode. Then in the forward mode, hexane was run at a flow rate of 6 mL/min for about 15 min or until the baseline on the integrator was stabilized. Regeneration of the column using the reactivation agent was done once every 2-3 weeks for about 8 h at the flow rate of 2 mL/min in the backflush mode. The column was then reconditioned using isopropanol and methylene chloride, and finally, hexane (as previously described). The pressure reading in the liquid chromatograph was about 2 MPa.

Computer Integrator Program

The computer integrator program for SAR separation is given in Table 4. Switching the valve backward and then forward was done manually. A typical chromatogram of the separated SAR fractions is presented in Figure 1.

Table 2. Solvent Delivery Program of Grizzle and Sablotny[1] for HPLC SAR Separations

Sector	Original Time (min)	Flow (mL/min)	Hexane	$MeCl_2$
Original Equilibration	10	6	100	0
1	3	6	100	0
2	4	8	85	15 linear
3	10	8	70	30 linear
4	8	10.0	10	90 back flush
5	5	9.0	100	0

Table 3. Modified Solvent Delivery Program for HPLC SAR Separations used in the Current Work

Sector	Original Time (min)	Flow (mL/min)	Curve	Hexane	$MeCl_2$	Curve
Equilibration	2.0	6.0		100	0	
1	6.0	6.0		100	0	
2	4.0	8.0	1.0	85	15	1.0
3	10.0	8.0		70	30	1.0
4	8.0	9.9	0.4	10	90	0.4
5	5.0	9.9		10	90	
6	15.0	9.9		100	0	0

Table 4. P.E. LC100 Method for HPLC SAR Separation

% Method 4: GRIZ1 Save Files: Both							
Data Coll	St. Time 0.00	End Time 40.00	Peak Width 5	A Sens 10000	B. Sens 10	S. Sens 0.00	B Code 2
Quant	Print Tot 0.0	Factor 1.0					
Plotter	Plot yes	Chart 10	Attn 1024	Offset 5	Plot RT Yes	Tic Mrk No	Plot Er Yes
Events	Ev Time	Ev Type	Value	Ev Name			
	0.000	R1Y4	Closed	INT On			
	0.001	R1Y3	Closed	RI ON			
	0.002	R1Y2	Open	UV OFF			
	5.400	R1Y3	Open	RI OFF			
	5.401	RLY2	Closed	UV ON			

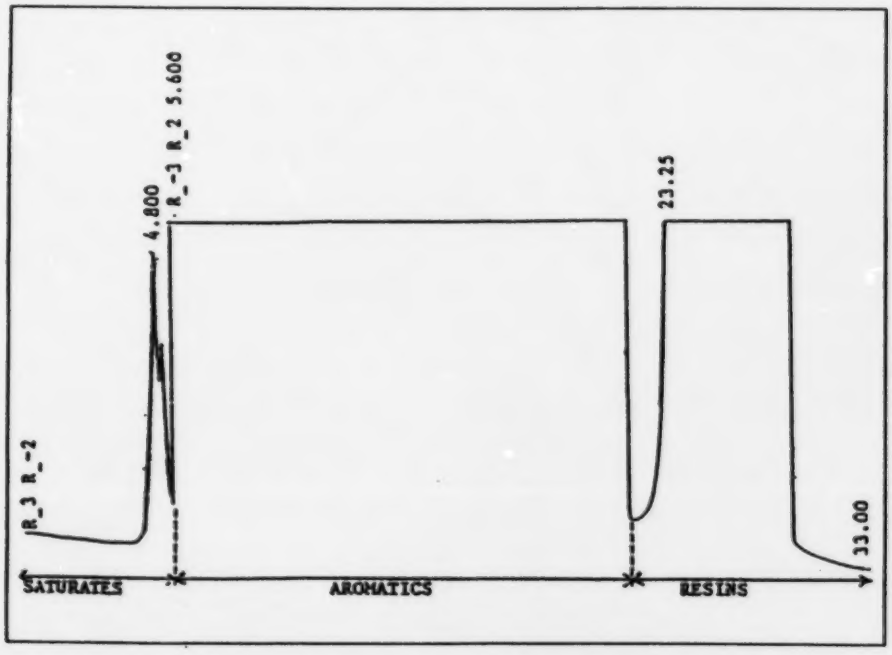

Figure 1. Typical Chromatogram Showing the Separation of a Maltene (62 mg, 1 mL Injection Loop, Sample Solvent-Hexane)

Gravimetric Procedures for Separated Fractions

Collection of the saturates began immediately after injection into a 50-mL round-bottomed flask and continued until 5.4 min had elapsed. The cutoff point for the saturates was chosen after a series of experiments had been performed to verify a clean separation from aromatics. Collection of the aromatic fraction began at this point in a 250-mL round-bottomed flask and continued until the end of the third sector. Resins were collected during the fourth and fifth backflushing sectors in a 250-mL round-bottomed flask. The saturates were rotor-evaporated for 2 min at 70°C and 380 mm Hg vacuum, the aromatics for 5 min at 70°C and 640 mm Hg vacuum, and the resins for 8 min at 70°C. The concentrated fractions were then transferred volumetrically to pre-weighed aluminum dishes using pentane for saturate and aromatic fractions and methylene chloride for the resin fraction. The transferred fractions were then left on a bench to evaporate for two hours at room temperature and pressure and weighed.

A different evaporation technique was tried using a vacuum pump. The nature of the aluminum dish however proved inconvenient. When kept in the vacuum desiccator it apparently resulted in spillage and loss of sample. The evaporation technique previously explained was, therefore, applied to all the fractions.

The material balance of the oil sample was calculated using the following definitions:

$$\% \text{ asphaltenes} = \frac{\text{weight of PPt}}{\text{original oil wt}} \times 100$$

$$\% \text{ maltenes} = 100 - (\text{asphaltenes wt } \%)$$

$$\text{wt maltene} = \text{original oil wt} - \text{wt asphaltene}$$

$$\text{wt of maltene injected} = \frac{\text{wt of maltenes (g)}}{\text{vol of hexane soln (ml)}} \times \text{vol of injection loop (ml)}$$

$$\%\ \text{wt fraction in maltenes} = \frac{\text{gravimetric wt of fraction}}{\text{injected maltene wt}} \times 100$$

$$\%\ \text{fraction in crude oil} = \frac{\%\ \text{wt maltenes} \times \%\ \text{wt of fraction in maltenes}}{100}$$

% recovery of maltenes = sum of % wt SAR fractions

% recovery of total oil = sum of % fractions in crude oil

B. Modified Syncrude Method

The Syncrude method, adopted from Bulmer and Starr,[3] was modified by replacing benzene with toluene as the solvent.

For a quick reference the summary and precision of the original Syncrude method is given below:

A sample of bitumen is dissolved in an equal volume of benzene. Forty volumes of n-pentane are added for each volume of benzene. The resulting precipitate is collected by filtration and weighed as asphaltenes. The filtrate is refluxed on a recycle adsorption apparatus packed with Attapulgus clay while the saturates and aromatics are carried to the kettle. The resins are eluted from the Attapulgus clay with methyl ethyl ketone and tetrahydrofuran containing 5% water by volume. Separation of the saturates and aromatics is performed on a chromatographic column packed with alumina and silica gel. The saturates and aromatics are eluted with n-pentane and benzene repectively. Any resin which may have remained is eluted with methyl ethyl ketone. All fractions are determined gravimetrically after evaporation of the solvent.

The following data based on 6 determinations illustrates the typical precision associated with a SARA analysis for a bitumen sample.

	Mean Value (wt %)	Standard Deviation (wt %)	Relative Standard Deviation
Asphaltenes	17.18	±0.19	1.11%
Resins I	38.99	±0.77	1.97%
Resins II	5.85	±0.25	4.27%
Saturates	16.87	±0.10	0.59%
Aromatics	18.27	±0.58	3.17%
Overall Recovery	97.16	±0.82	0.84%

2.4 Analysis of SAR Fractions for Cross-Contamination in the HPLC Method

Cross-contamination of the SAR fractions obtained from the different separation methods was examined by reinjecting the fractions into the HPLC. For instance the saturate fraction, separated using the HPLC system, was reinjected into the HPLC and the chromatogram was observed for cross-contamination. In a similar way, the aromatic fractions were also reinjected and tested for cross-contamination. Calibration to estimate weight percent contamination was performed. The details are as follows: 32 mg of maltenes were injected into the HPLC using a 1-mL injection loop. The SAR fractions were collected and freed from solvents as described in Section 2.3. The aromatic fraction was weighed then diluted to 10 mL. One mL of the solution (W_{A_1}) was injected using a 1-mL injection loop. The chromatogram of this fraction was examined and the peak area of the aromatics in the aromatic fraction was measured (P_{AA_1}). The ratio of the peak area of the aromatics in the aromatic fractions to weight injected gives the response factor of the aromatics. Similarly, the resin fraction was diluted and reinjected (W_{R_1}) and its chromatogram studied. The ratio of the peak area of the resins (P_{AR_1}) in the resin fraction to the weight injected gives the response factor of the resins. The peak area of the resins in the aromatic fractions was observed, and used with the response factor of the resins to calculate the weight percent contamination of resins in aromatics.

Similarly, the weight percent contamination of aromatics in the resin fraction was calculated. The following equations were used for calculating weight percent contaminations.

P_{AA_1} = peak area of aromatics in aromatic fraction

W_{A_1} = weight of aromatic fraction injected

$$R_A = \frac{P_{AA_1}}{W_{A_1}} = \text{response factor of the aromatics}$$

P_{AR_1} = peak area of resins in resin fraction

W_{R_1} = weight of resin fraction injected

$$R_R = \frac{P_{AR_1}}{W_{R_1}} = \text{response factor of the resins}$$

P_{AA_2} = peak area of aromatics in resin fraction

$$W_{A_2} = \frac{P_{AA_2}}{R_A} = \text{weight of aromatics in resin fraction}$$

P_{AR_2} = peak area of resins in aromatic fraction

$$W_{R_2} = \frac{P_{AR_2}}{R_R} = \text{weight of resins in aromatic fraction}$$

Therefore $\frac{W_{A_2}}{W_{R_1}} \times 100 = \text{weight percent aromatics in resins}$

and $\frac{W_{R_2}}{W_{A_1}} \times 100 = \text{weight percent resins in aromatics}$

Aliphatic and aromatic contents of the SAR fractions obtained from the two different methods (HPLC and Syncrude) were examined by ^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR). The data are reported in the Results section.

2.5 *Spectroscopic Instrumentation Application*

A. Analysis of Specially Cleaned Oil Using Gas Chromatograph/Mass Spectroscopy (GC-MS)[6]

Solutions were prepared by dissolving oil samples (2.0 g) in 5.0 mL tetrahydrofuran. Three µL of this solution were injected into the heated injection port (290°C) of the gas chromatograph. The split ratio was set at 8:1 measured at 35°C (column temperature). The column head pressure was set at 300 kPa. Part of the mixture solution was passed through a 50 m, cross-linked methyl silicon gum (PONA) capillary column with inside diameter of 0.2 mm and film thickness of 0.5 microns. The column was operated at 35°C for 14 minutes, then temperature programmed at 10°C min^{-1} to 240°C, and held there for 10 minutes.

The separated products were detected by a HP 5970A mass selective detector. The temperature of the ion source was 250°C. The mass spectra were obtained with 70 electron volt (ev) ionization energy. The temperature of the GC-MS interface was 190°C. The mass range scanned was 35-300 atomic mass unit (amu). Other parameters were threshold at 20 linear counts, scan speed at 690 amu/s, and sample peak threshold at 300 triggered on total abundance.

The spectra were recorded on a magnetic tape operated by a HP 9825 computer. Two analyses were completed for each sample. For the first analysis, the mass detector was turned on at 14:00 min and off at 25:00 min, with the electron multiplier set at 200 v (autotune value). For the second analysis, the mass detector was turned on and off at 25:00 and 44:50 min, respectively, with the electron multiplier set at 1600 v.

B. Analysis of SARA Fraction Using NMR (^1H and ^{13}C)[6]

The ^1H NMR spectra were recorded on a 200 MHz Bruker AC-2 200 ZNP spectrometer using the Fourier transform pulsed technique with a pulse width

(90°C) of 7.6 μs, an acquisition time of 1 s, a spectral width of 4032 Hz and 4-32 scans. Concentrations of oil samples were in the range of 15-40% (wt/vol) in $CDCl_3$. Chemical shifts were measured relative to tetramethylsilane (TMS) at 24°C. The ^{13}C NMR spectra were recorded with the same spectrometer using the Fourier transform pulsed technique with a pulse width (90°C) of 5.6 μs, an acquisition time of 1.31 s, a spectral width of 12.5 KHz, a pulse delay of 2 s, NOE suppression broad band decoupling, and 4000-25,000 scans. The concentrations of the oil samples were as stated previously. Chemical shifts measured relative to TMS at 24°C in the presence of the relaxation agent chromium triacetylacetonate ($Cr[acac]_3$).

3. RESULTS

The source and type of oil samples examined in the current investigation are described in the Experimental section of this report. The tables are compiled in Appendix A. The more important summary figures and tables are presented in the main text of the report.

The overall results presented on a task basis are detailed below.

Task 1 - SARA Development Work

In this task, 12 oil samples were examined by the HPLC technique. Two oil samples were examined by liquid column chromatography using the Syncrude method. The origin of the samples is described in the Experimental section (Table 1). The weight percent of asphaltenes and maltenes, the material balance, as well as the precision of the oil samples examined are given in Table A1. A summary of the results for the above maltenes and their HPLC separated fractions are given in Table 5.

The corresponding results for the Syncrude method compared with the HPLC results are given in Table 6. In Table A2 the reproducibility and material balance of the Syncrude method can be compared against time for oil samples 1-21 and 9-16. The material balance and separation consistency results of the HPLC and Syncrude methods for these two samples are compared in Tables A3 and A4.

Gas chromatography tests were conducted on a solvent containing saturate and aromatic fractions of two oil samples, 16-16 and D16-16. The results are given in Table A5.

Nuclear magnetic resonance analysis was conducted on 12 oil SAR fractions, four asphaltene fractions and one crude oil. The results of the HPLC SAR fractions for the proton NMR are given in Table 7, and for carbon thir-

Table 5. Weight Percent Determination of SARA Fractions in Murphy Eyehill Oils

Sample	1-21			9-16			16-16			D16-16		
	May/87	Jan/89	June/89	May/87	Jan/89	June/89	May/87	Jan/89	June/89	May/87	Jan/89	June/89
Saturates	25.1 ± 0.2	25.5 ± 0.1	26.3 ± 0.5	24.4 ± 0.1	25.7 ± 0.2	24.7 ± 0.3	25.8 ± 0.3	25.5 ± 0.3	26.3 ± 0.7	23.5 ± 0.2	24.5 ± 0.2	25.5 ± 0.5
Aromatics	45.9 ± 0.6	48.4 ± 0.2	48.4 ± 0.4	46.0 ± 0.3	46.7 ± 0.2	47.0 ± 0.3	47.1 ± 0.2	48.7 ± 0.2	48.0 ± 0.2	47.8 ± 0.2	48.2 ± 0.1	49.9 ± 0.3
Resins	13.4 ± 0.2	13.4 ± 0.1	13.6 ± 0.2	11.5 ± 0.2	16.5 ± 0.1	11.9 ± 0.2	13.6 ± 0.1	11.4 ± 0.2	11.9 ± 0.2	12.2 ± 0.1	13.1 ± 0.1	13.5 ± 0.3
Asphaltenes	14.4 ± 0.4	12.5 ± 0.2	12.3 ± 0.1	10.0 ± 0.1	10.4 ± 0.5	10.0 ± 0.2	15.1 ± 0.3	12.8 ± 0.4	13.2 ± 0.4	13.3 ± 0.1	13.2 ± 0.5	12.7 ± 0.1
Recovery Total Wt %	98.8 ± 0.8	99.8 ± 0.3	100.6 ± 0.5	91.9 ± 0.4	99.3 ± 0.6	93.6 ± 0.5	101.6 ± 0.5	98.4 ± 0.6	99.4 ± 0.8	96.8 ± 0.3	99.0 ± 0.6	101.6 ± 0.7

Number of determinations are 3-4 per fraction. Errors are estimated standard deviations. Ref. "Applied Mathematics for Physical Chemistry," J.R. Barrante, Prentice Hall Inc. (1974) pp. 129-133.

Table 6. Weight Percent Determination of Maltene Fractions, Murphy Eyehill Oils 1-21 and 9-16, June 1989 - Comparison of Two Different Methods

Sample	1-21		9-16	
	HPLC*	Syncrude	HPLC*	Syncrude
Saturates	26.3	33.8	24.7	37.0
Aromatics	48.4	36.3	47.0	34.7
Resins	13.6	14.6	11.9	14.4
Asphaltenes	12.3	11.7	10.0	10.9
Total Wt Recovery	100.6	96.4	93.6	97.0

*Number of determinations are 3-4 per fraction.

Table 7. Percent Aromatic and Aliphatic Protons in the Four Murphy Well SAR Fractions According to ^1H NMR Analysis

Collection Date	Fractions	1-21		9-16		16-16		D16-16	
		Aromatics	Aliphatics	Aromatics	Aliphatics	Aromatics	Aliphatics	Aromatics	Aliphatics
May/87	Saturates	0	100	1.3	98.7	0	100.0	0.4	99.6
	Aromatics	7.7	92.3	6.7	93.3	5.3	94.7	9.5	90.5
	Resins	7.2	92.8	4.1	95.9	4.0	96.0	3.0	97.0
Jan/89	Saturates	0	100	0	100	0	100	0	100
	Aromatics	8.0	92.0	6.0	94.0	9.8	90.2	5.0	95.0
	Resins	5.1	94.9	3.5	96.5	5.0	95.0	7.0	93.0
June/89	Saturates	0	100	0.2	99.8	0	100.0	0	100.0
	Aromatics	8.0	92.0	7.6	92.5	11.7	88.3	5.2	94.8
	Resins	5.7	94.3	6.1	93.9	2.8	97.2	6.9	93.1

teen NMR in Table 8. Also the calculated ratios of aliphatic and aromatic protons are compiled in Table A6. Data for the same ratios for the carbon NMR are listed in Table A7. Because of the great interest in the possible compositional changes in resins, their aliphatic to aromatic proton and carbon ratios have been calculated. The results are given in Tables A8 and A9, respectively. The NMR data for the four asphaltene fractions are presented in Table 9.

Proton and carbon thirteen NMR tests were conducted on selected Eyehill oil SAR fractions (1-21 and 9-16) obtained by the Syncrude method. The results are compared with the data of the HPLC separated fractions in Tables A10 and A11. NMR results for the crude oil (1-21) are given in Table A13.

Task 2 - GC-MS Development Work

In this task, eight oil samples from Murphy's Eyehill reservoir collected in sets of four at six-month intervals were analyzed by GC-MS. After a systematic and careful analysis of the GC-MS spectra, the peaks common to both primary and fireflood samples were eliminated, and the remaining peaks found in only some of the fireflood oil samples were compiled (Table 10). Toluene was demonstrably absent in all GC-MS experiments for oil 1-21.

The common components found in all oil samples are summarized in Table 11.

Table 8. Percent Aromatic and Aliphatic Carbons in the Four Murphy Well Sample SAR Fractions According to ^{13}C NMR Analysis

Collection Date	Fractions	1-21		9-16		16-16		D16-16	
		Aromatics	Aliphatics	Aromatics	Aliphatics	Aromatics	Aliphatics	Aromatics	Aliphatics
May/87	Saturates	1.7	98.3	0.7	100	0	100	0	100
	Aromatics	41.4	58.7	33.3	66.7	23.5	76.5	33.2	66.8
	Resins	51.4	48.6	39.6	60.4	21.1	78.9	29.9	70.1
Jan/89	Saturates	0	100	0	100	0.6	99.4	0	100
	Aromatics	30.0	70.0	32.7	67.3	30.3	69.7	25.9	74.1
	Resins	33.6	66.4	22.2	77.8	24.7	75.3	33.7	66.3
June/89	Saturates	0	100	0	100	0	100	0	100.0
	Aromatics	33.8	66.3	44.8	55.2	41.4	58.6	29.1	70.9
	Resins	35.3	64.3	38.7	61.3	50.0	50.0	27.2	72.8

Table 9. Percent Aromatic and Aliphatic Protons and Carbons in Asphaltenes Obtained from Murphy Oil Samples of June 1989 According to ^{1}H and ^{13}C-NMR Analysis

Asphaltene Sample	Proton			Carbon 13		
	Aromatics	Aliphatics	H_{Al}/H_{Ar}	Aromatics	Aliphatics	C_{Al}/C_{Ar}
1-21	10.5	89.5	8.52	45.7	54.3	1.18
9-16	10.9	89.1	8.17	46.1	53.9	1.16
16-16	11.5	88.5	7.69	40.5	59.5	1.46
D16-16	8.4	91.6	10.90	42.5	57.5	1.35

Table 10. Selected GC-MS Oil Components Found Only in Some of the Fireflood Oil Samples

Name	Well No.	Rel. Abundance	
		Jan/89	June/89
n-octane	9-16	80.7	89.1
	16-16	64.9	44.0
Toluene	9-16	65.4	62.5
	16-16	35.3	40.2
	D16-16	29.4	72.9
2-methyl octane	9-16	41.0	47.5
	16-16	32.3	4.0
Ethylbenzene	9-16	39.6	43.8
	16-16	30.2	33.5
m and p-xylenes	9-16	98.4	98.7
	16-16	63.0	64.7
o-xylene	9-16	67.3	66.9
	16-16	48.1	43.7
n-nonane	9-16	100.0	100.0
	16-16	80.1	71.1
Nonyne	9-16	34.0	N.D.
	16-16	17.5	N.D.
Chlorotoluene	9-16	20.0	19.1
	16-16	34.5	N.D.
1-methyl-3-ethylbenzene	9-16	68.6	63.1
	16-16	35.1	33.9
Trimethylcyclohexane	D16-16	24.1	12.6
Heptene	D16-16	29.6	28.8

Table 11. Selected GC-MS Common Oil Components

Name	Well No.	Rel. Abundance	
		Jan/89	June/89
2-or 4-ethyl-1-hexene	1-21	15.5	14.5
	9-16	16.3	17.5
	16-16	5.8	7.6
	D16-16	14.0	14.0
1,1,3,3, tetramethylcyclopentane	1-21	12.7	12.6
	9-16	6.2	7.4
	16-16	32.6	28.7
	D16-16	26.8	27.9
1-trans-2-trans-4-trimethylcyclohexane	1-21	25.1	23.1
	9-16	30.2	32.7
	16-16	32.6	28.7
	D16-16	26.8	27.9
1,3,5-trimethylcyclohexane	1-21	21.6	21.4
	9-16	7.5	9.5
	16-16	15.9	10.9
	D16-16	-	21.0
1-Methyl-2 or 3-ethylcyclohexane	1-21	10.1	8.9
	9-16	4.0	15.1
	16-16	5.6	7.0
	D16-16	-	9.0
Diethylcyclohexane	1-21	40.2	43.2
	9-16	23.2	26.5
	16-16	37.0	31.5
	D16-16	43.1	40.5
Nonyne	1-21	56.1	53.4
	9-16	-	-
	16-16	41.7	-
	D16-16	51.6	51.7
Diethylcyclohexane	1-21	14.4	16.1
	16-16	7.7	18.0
	D16-16	14.2	16.3

4. DISCUSSION AND CONCLUSIONS

4.1 Discussion of Source Materials, Asphaltenes and Maltenes

Separation of the crude oil into asphaltenes and maltenes was performed by the method described in the Experimental section. The solution of the crude oil in pentane was left for at least 2 h before the filtration step (after 2 h no considerable change in asphaltene content was observed). The asphaltenes from the various wells were studied for reproducibility. The results, as shown in Table A1, revealed the suitability of the technique. Sources of errors for the asphaltene determination might arise from handling the fractions (asphaltenes and maltenes). Also, there should be a unified drying time for the asphaltenes as well as the maltene fractions. It should be noted that the color of the asphaltenes varies from dark brown to black, but no discrepancy in reproducibility of yield was observed.

Maltenes can be determined by two methods. The first method used and later dropped was to evaporate the solvent from the maltenes. A high vacuum rotor evaporator was used and the maltenes weighed. This method had two shortcomings: (1) not all of the solvent (pentane) could be removed from the maltenes resulting in more than 100% recovery, and (2) evaporation caused the loss of light ends resulting in poor material balance data. This method was rejected. The second method comprised the determination of the maltene content from the asphaltenes content by subtracting the asphaltene weight from the oil weighed. The asphaltene determination technique was very reliable and reproducible, which resulted in insignificant error for maltene determination.

4.2 Discussion of SAR Separation Method by HPLC

Previous work reported by Grizzle and Sablotny[1] was conducted on 57 model compounds (30-60 mg in 270-450 µL injection loop) where distinctive separation of saturate and aromatic compounds could be seen. Their work did not show the exact cutoff points of the saturate, aromatic and resin frac-

tions of petroleum oil or maltenes. But their reproducibility was better than 2% for any compound class group type fractions.

The reproducibility of the HPLC method was very good (Table 5). The material balance was also very good with the exception of three samples (9-16, May/87 and June/89; D16-16, May/87). These samples showed some loss of material, most likely from the saturate and aromatic fractions. The gravimetric loss might be caused by evaporation where the light ends disappear, as shown by the gas chromatogram. The evaporated and the non-evaporated saturate and aromatic fractions were analyzed by GC simulated distillation. This showed at the boiling point of ≈205°C the loss to be ≈15 wt % for saturates, and ≈2.5 wt % for aromatic fractions. To account for the material balance deficit, about 85% of the loss can be assigned to the saturate fraction and ≈15% to the aromatic fraction.

The response factors, calculated by reinjecting the aromatic and resin fractions, are 1.6×10^9 counts/mg for the aromatic fraction and 2.3×10^9 counts/mg for the resin fraction. In our analysis (HPLC method) there was less than 1% by weight cross-contamination of aromatics in saturate fraction or resins in aromatics, and no cross-contamination of aromatics in resins. When the purity of the separated fractions is tested by NMR spectroscopy, the aromatic cross-contamination in the saturate fractions is from zero to less than one percent. But the reinjection of the fraction is a more sensitive method than the NMR technique for identifying the cross-contamination of the fractions. Reinjection of fractions is very time consuming, however, and a scaled-up gravimetric method is required to obtain more accurate response factors for these fractions. The time required for separation using the HPLC technique is about 50 min per run. The total amount of solvents per run is about 500 mL. The problems and limitations of the technique might be noticed when one considers the sample size. In our technique, 30-68 mg of maltenes of SAR fractions were used per run. This sample size is far less than that used for the Syncrude method. About 30 g per separation per two days are used for the Syncrude method. Moreover, the column life may not be as long as that reported by Grizzle and Sablotny,[1]

(more than 500 samples). In our case, the column started to deteriorate after about 200 injections.

Finally, the gravimetric error, which resulted from the evaporation of the light ends and/or retention of the solvents, could possibly be improved by using the vacuum oven for evaporation. The use of the correction factor of 15% for aromatics and 85% of saturates (based on GC simulated distillation estimate on injected evaporated and non-evaporated saturate and aromatic fractions) could be used to achieve 100% material balance.

4.3 Discussion of Other Method (Syncrude) in Comparison to the HPLC Method

The reproducibility of data reported for the Syncrude method was good.[3] The material balance obtained from this method is average and is comparable to the HPLC method. The results of the SAR fractions from the two methods, however, are different (Table 6). In the Syncrude method (Figure 2) for well 1-21, the aromatics constitute the highest percentage of the oil followed by saturates and then resins. Whereas for well 9-16 (Table 6), the saturates constitute the highest percentage of the oil followed by aromatics and then resins. The weight percentages of the saturates and the resins in the Syncrude method are much higher than those from the HPLC method. Moreover, the percentages of the aromatics in the Syncrude method are lower than the HPLC method.

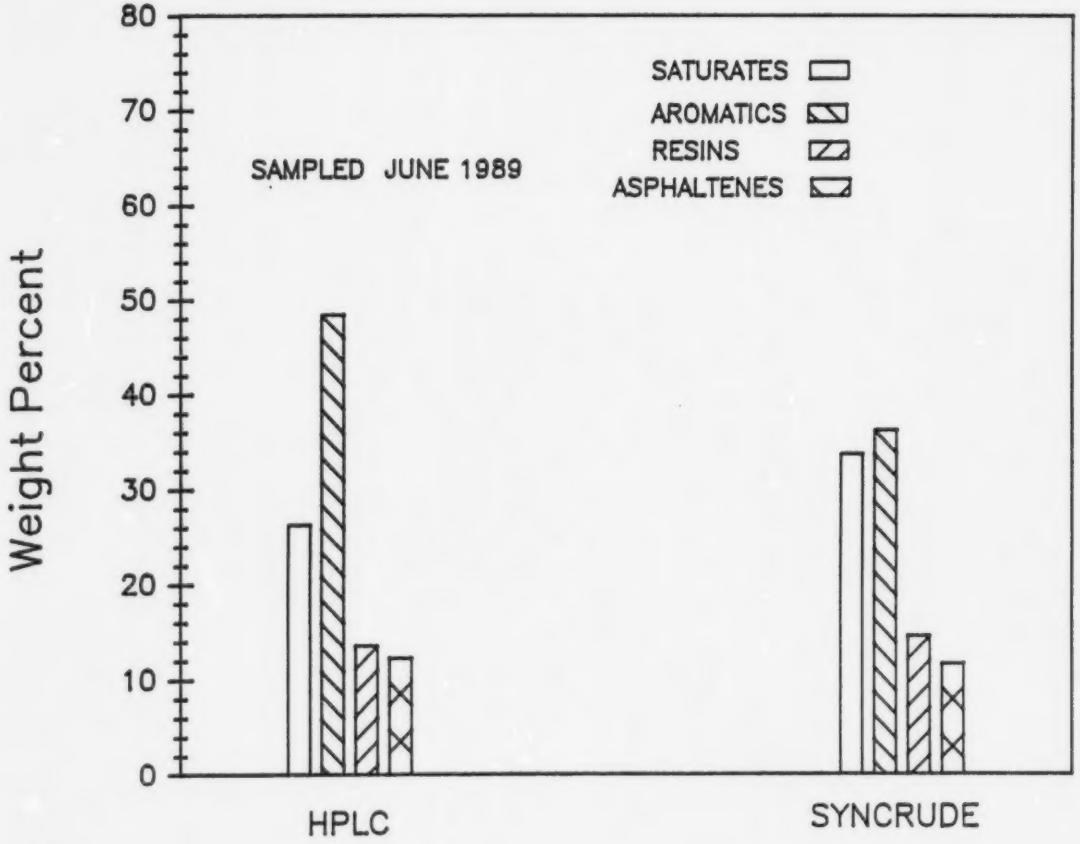

Figure 2. SARA Yield of Oil 1-21 Separated by Different Methods

With regard to purity, the saturate fractions obtained by the Syncrude method show significant aromatics cross-contamination. This was tested by reinjecting the indicated amounts of the fractions obtained by the two different methods (Table A12). The largest cross-contamination was found in the Syncrude (10.2 wt %), and the lowest in the HPLC separated saturates (3.0 wt %). It should be noted that these are not absolute values, but rather a relative measure of the aromatics contamination. The type of aromatics found in the saturate fraction (presumably low molecular weight mono and diaromatics) do not represent the extinction coefficient (E_a) given by the neat aromatic fraction (containing also the higher molecular weight polyaromatics) used to calculate the response factors. Thus, the true response factor may be in error to varying degrees. In order to obtain a correct response factor, it is necessary to isolate and weigh the cross-contaminants using the HPLC technique. Of course, this is not possible for the HPLC separated saturate fraction (only 3% of 1.9 mg) without scaling up the injected maltene concentration by at least an order of magnitude. But, the NMR data may be used to estimate a more realistic (absolute) value of the cross-contamination in these fractions. When the ^{13}C NMR data are compared to the three methods for the saturates, it is seen (Tables A10 and A11) that the aromatics content for the HPLC separated saturates is zero, for Syncrude between 2.7-4.7%. If we accept this as a realistic value for cross-contamination, then the reinjected saturates response factor is in error by a factor of 3. Although the Syncrude method has merits in using large-scale preparative separations compared to the HPLC, the significant aromatic content in the saturate fraction would be an obstacle for further detailed analysis of these fractions. As well, the Syncrude used only single SARA determinations in the current work and therefore the precision of the gravimetric values are unknown. Thus the large variations observed in the results against time (Table A2) may be due to either the experimental technique of the method and/or real changes in the SARA composition of the oil. Because of this uncertainty in single determined SARA values, the Syncrude method for monitoring compositional changes in the oil is not a suitable technique. From a time and cost perspective, the multiple SARA determination per sample by this method is not practical.

4.4 Discussion of the Application of Asphaltenes and SAR Fractions Analysis Separated by HPLC Method

Assuming external factors such as sample contamination is not present, this method is reliable and suitable for detailed analysis (liquid chromatography for mono-, di- and polyaromatics; infrared spectroscopy for ketones, etc.; NMR for various significant peaks; and GC-MS for alkanes or new products produced by fireflood effects). The Syncrude method has considerable aromatics in the saturate fraction. Loss of mono-, di- and possible triaromatics from the aromatic fraction would make the saturate and aromatic fractions unsuitable for further analysis.

Comparison of SARA gravimetric data was not very conclusive. This is because of the continuous change in oil composition and the lack of production data for the wells. The time effect is apparent even for the "primary" oil (well 1-21; Table 5). For example, a difference was observed for the aromatic and asphaltene yields of well 1-21 between the May 1987 and January 1989 collected samples, and also the resin yield of well 9-16. Similar observations were made for well 16-16 between May 1987 and January 1989 for asphaltene and resin fractions. Moreover, the resin yields of well D16-16 between May 1987 and May 1989 and the aromatic yield of the same well of June 1989 showed a difference.

The compositional differences of the wells were also studied in terms of the SARA NMR data. It was observed that interwell differences in the four wells were fairly significant in the variations of the aromatic ^{1}H and ^{13}C NMR and somewhat less variations in the resins ^{1}H and ^{13}C NMR values (Tables 7 and 8). Also some differences were observed in the asphaltene composition (Table 9 and Figure 3).

The time effect in terms of NMR data also revealed a compositional change in the wells. For example, the aromatic protons in the resin fraction dropped dramatically for well 1-21 between 1987 and 1989 (Table 7). A large increase in the aromatic protons of the resin fraction was observed

for well 9-16 during the same period. Similar observations were made for wells 16-16 and D16-16. The results from carbon ^{13}NMR analysis also revealed similar trends. Taking as an example the aromatics ^{13}C NMR data (Table 8, Figures 4 to 7), which illustrate the time effect on the oil composition changes.

In general, there are observable differences seen between the composition of the well oils, but there are significant compositional changes against time. These differences are real and not caused by variations in reproducibility of SAR fractions using the HPLC technique. The changes in the ratios of proton aliphatic to proton aromatic and carbon aliphatic to carbon aromatic possibly indicate two main effects (Tables A6 and A7). The first could be a dilution effect caused by distillation or pyrolysis products as a result of cracking. A combined effect of distillation and cracking could cause the ratio of proton aliphatic to proton aromatic to increase. The second, the condensation effect (coking), results in lowering the ratio of the carbon aliphatic to carbon aromatic. Cracking the long side chains of aromatic molecules causes the ratio to go down when the shorter chained substituted aromatics elute a later date.

Crude oil 1-21 (June 1989) was also analyzed by NMR spectroscopy. The ^{1}H and ^{13}C NMR data are given in Table A13. In an attempt to see how the individual, separated SARA fractions would predict the NMR signals in the whole oil, a calculation was performed on the experimental SARA NMR results. The necessary data to do this were obtained from Table 5 (weight fractions of the constituents), Tables 7 and 8 (saturate, aromatic and resin fractions [^{1}H and ^{13}C respectively]) and Table 9 (asphaltene NMR values). From these considerations, Table A14 was constructed and the calculated oil NMR values were compared with those in Table A13. The result shows that for ^{1}H NMR the calculated oil signals are in excellent agreement with the experimental values for the whole oil. The computed aromatics value was ~4% lower and the aliphatics only 1% higher than the values from the direct experiments.

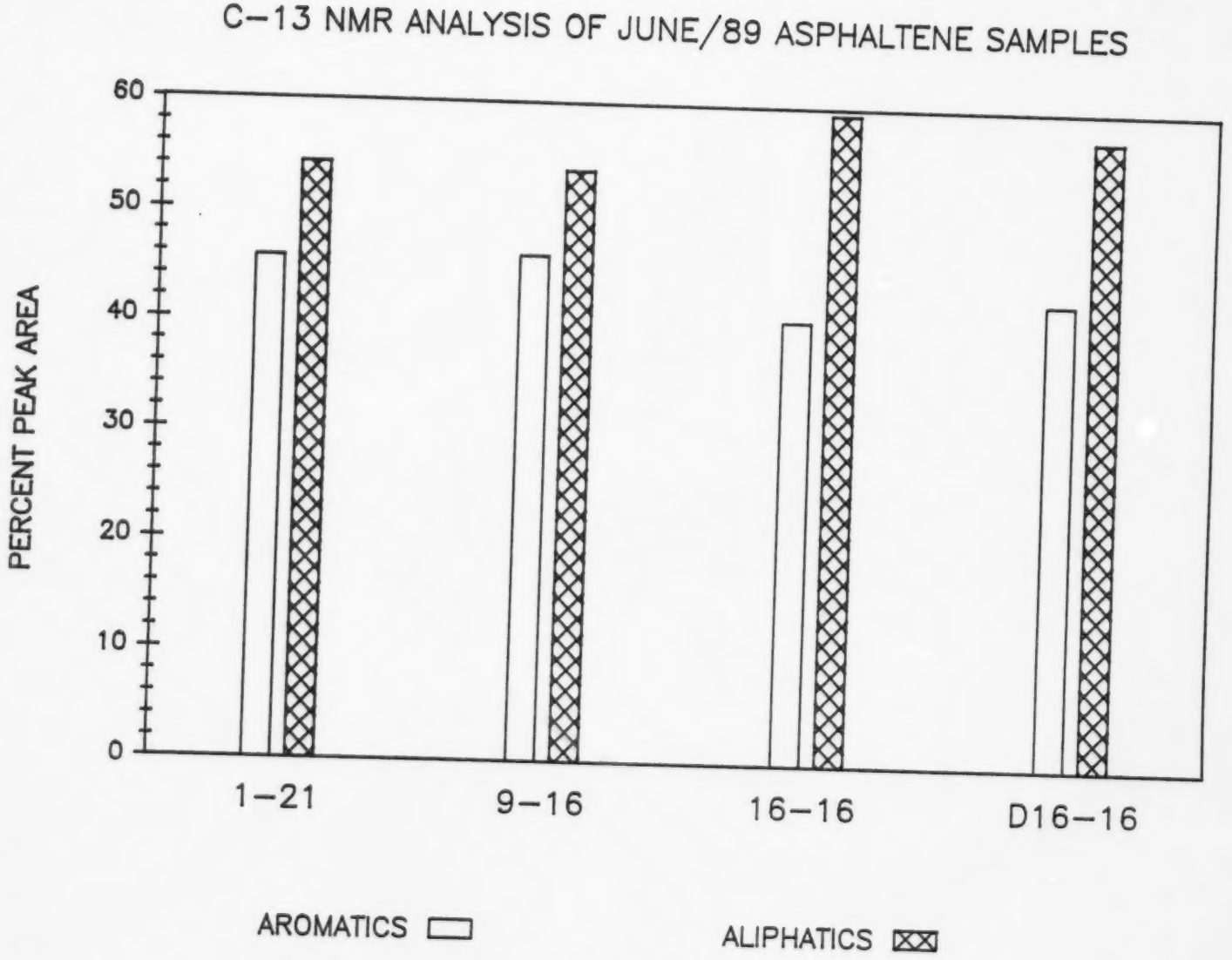

Figure 3. C-13 NMR Analysis of June/89 Asphaltene Samples

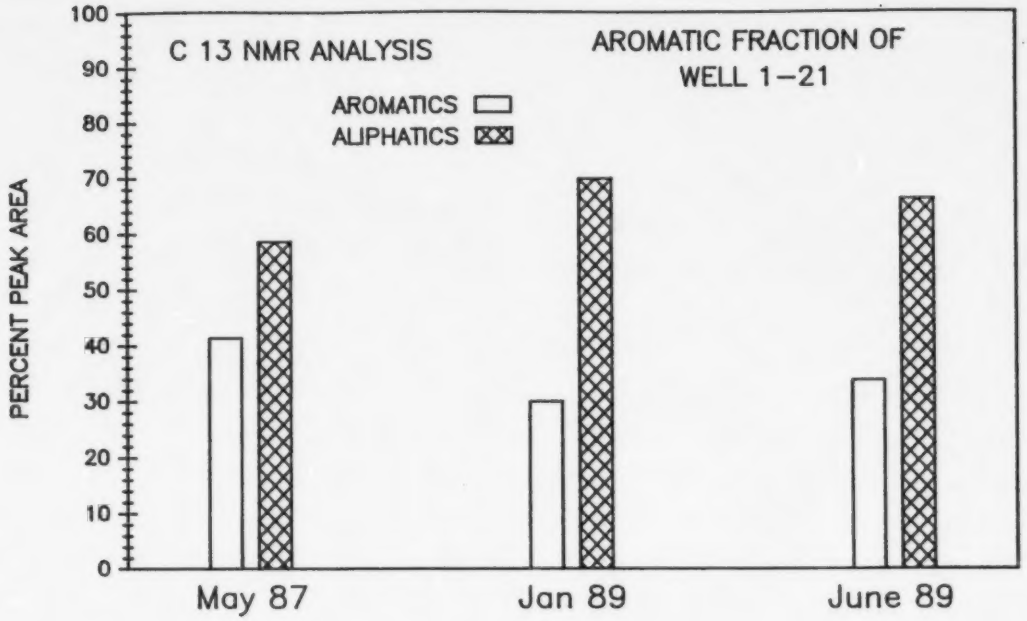

Figure 4. C-13 NMR Analysis of Aromatic Fraction of Well 1-21

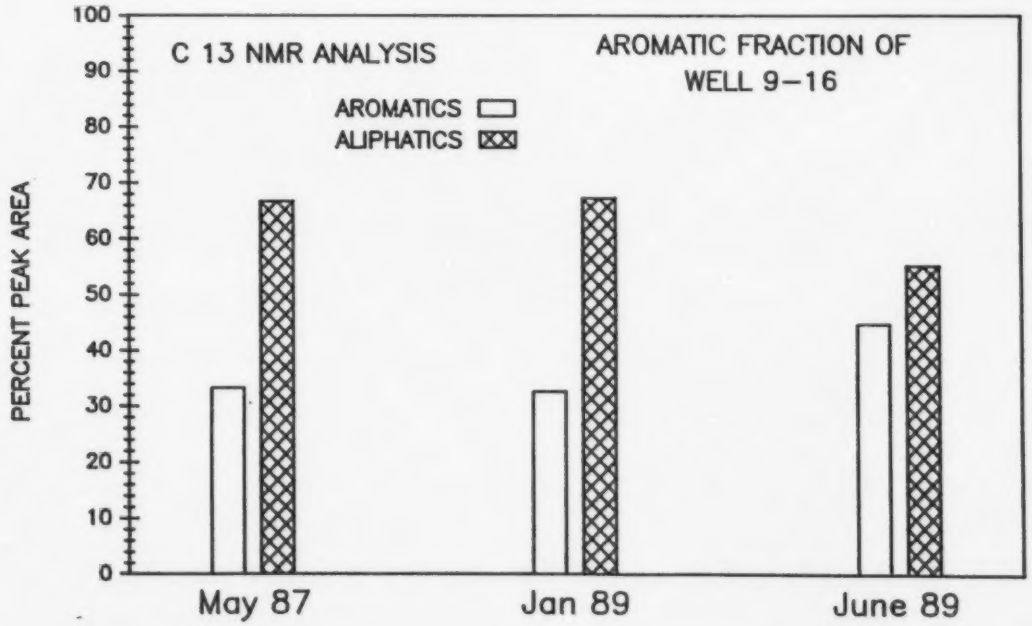

Figure 5. C-13 NMR Analysis of Aromatic Fraction of Well 9-16

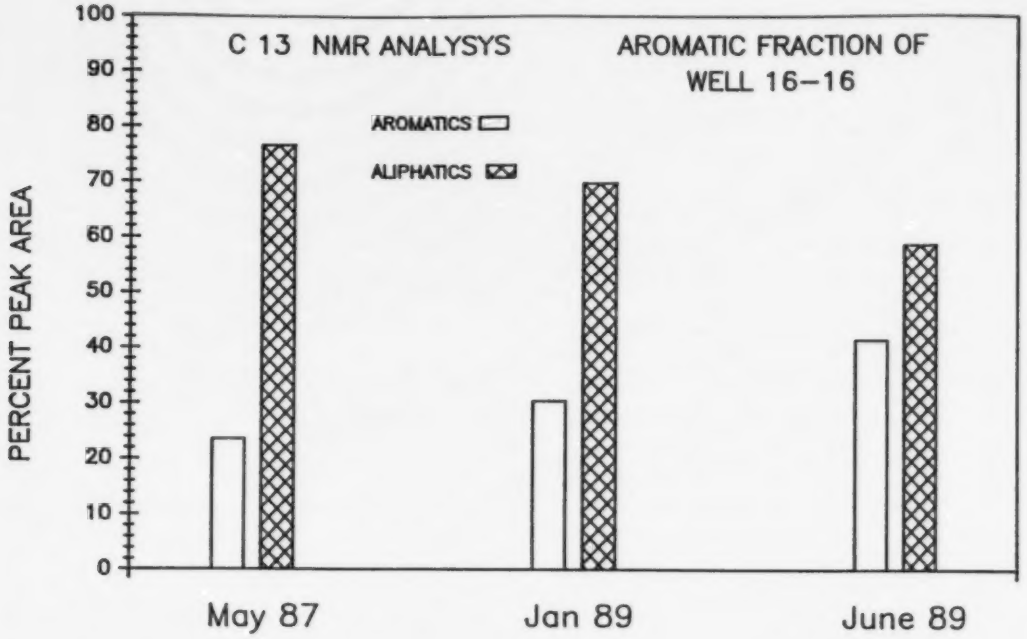

Figure 6. C-13 NMR Analysis of Aromatic Fraction of Well 16-16

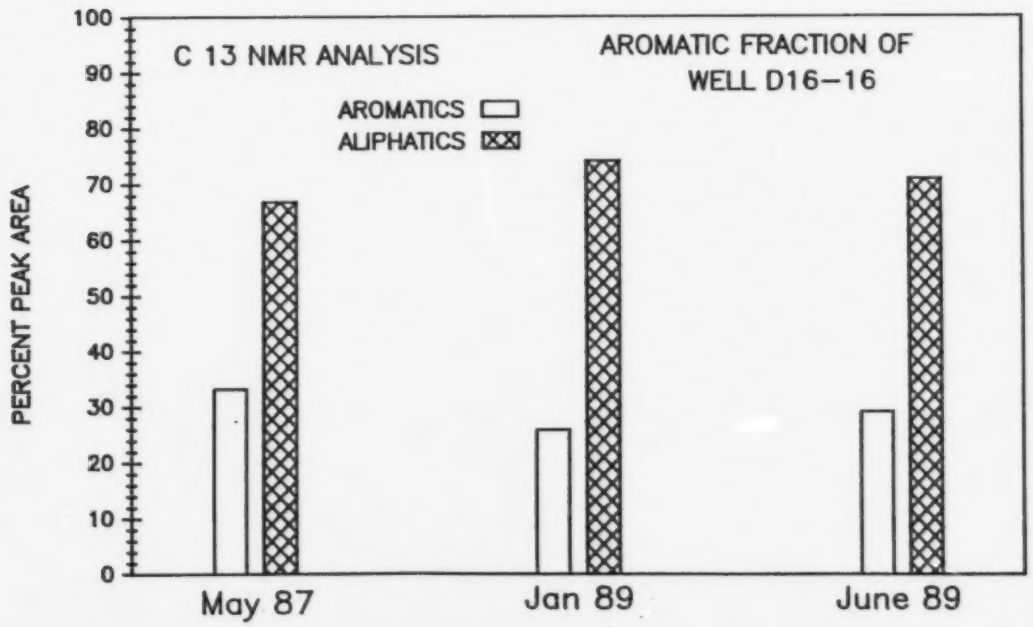

Figure 7. C-13 NMR Analysis of Aromatic Fraction of Well D16-16

In the case of ^{13}C NMR the discrepancy between computed and experimental values was large. The computed aromatics signal was ~37% higher and the aliphatics response was ~8% lower than the corresponding experimental values. The reason for this disagreement is unknown, but one explanation may be the poor noise to signal ratio for the aromatics ^{13}C NMR data. Another cause could be the low resolution spectrum where mixing of the aromatics and aliphatics signals occurred and are integrated with the aromatics. A follow-up study is necessary to resolve this problem, possibly using high resolution equipment, larger sample size, longer data collection time, and a larger number of oil-SARA NMR tests.

4.5 Discussion of GC-MS Results

The best evidence for fireflood effects in the oil samples examined (changes in composition caused by cracking reactions) is toluene, and a host of aliphatic isomers and short chain substituted benzenes, i.e. ethyl benzene, xylenes, etc. The differences between the fireflood samples indicated different stages of fireflood effects on the chemical compositions of the produced oil. The effect of time was observed for n-octane of well 16-16, toluene for well D16-16, methyl octane for well 16-16, nonyne and chlorotoluene for well 16-16, and trimethylcyclohexane for well D16-16 samples (Table 10). In the absence of more frequent and longer periods of monitoring, assignments and interpretation of these changes are difficult. An in-house combustion tube experiment sequence would be required to identify and quantify these effects.

In general the common peaks relative constancy with time (Table 11) as compared to the very large variations in some of the component concentrations found only in fireflood wells (Table 10) could make this method (if developed) very useful for monitoring process effects in produced oil.

This method would be very useful for the identification of changes in the SARA fractions. The development of a suitable computer program to manipulate the data quickly and produce tables and relative abundances of common and non-common compounds (those present only in the fireflood samples) is required.

5. RECOMMENDATIONS FOR FUTURE WORK

1. Maximize the lifetime of the HPLC analytical column by using a guard column (short length, 3-5 cm; narrow diameter, 2-4 mm) inserted between the injection valve and the analytical column. The guard column is usually filled with the material used in the analytical column. The purpose of this column is to trap components in the sample or mobile phase, which would normally be retained on the head of the analytical column. Once the material in the guard column has been contaminated, it is a simple matter to empty it and refill it with fresh material. The frequency at which the material must be changed depends on how many impurities are in the samples and mobile phases. In most cases this must be determined experimentally. More experiments should be performed with different polarity solvents (mixtures), such as tetrahydrofuran, methanol, etc., to regenerate or chemically clean the column. The re-activation agent used in the project showed little improvement and its whole composition was unknown.

2. Improve the gravimetric technique by replacing the aluminum dishes used for evaporating the solvents from the SAR fractions by a different container (a light, widely open jar or vial with a cup). This would avoid loss of sample and eliminate an extra step in the procedure. The separated fractions should be kept in the refrigerator to avoid moisture absorbance (the oil fractions might be hygroscopic). Also use a vacuum oven for the aromatic fraction to reduce retained solvents content.

3. Search in the SAR fractions for oxygenated molecules using analytical pyroprobe and HPLC fluorescence detection techniques.

4. Separate the aromatic fraction further by HPLC and suitable column/solvents into mono, di-, tri- and polyaromatic sub-fractions. Analyze these subfractions with GC-MS, NMR and fluorescence spectroscopy for oxygenated hydrocarbons.

5. Develop a computer program to quantify common and non-common peaks in the GC-MS spectra.

6. Scale up the method to obtain larger quantities of separated fractions.

7. Reinject larger quantities of SAR fractions obtained from different methods into the HPLC system and gravimetrically determine cross-contaminants in these fractions. Then determine the true response factors of the fractions and the contaminants.

8. For better accuracy and consistency, use photometry (at 600 nm) in the current gravimetric methods to determine asphaltene contents of the oil samples.

9. Generate a ^{1}H and ^{13}C NMR data bank for large numbers of oils and their SARA fractions. From the results, develop a technique to monitor compositional changes in EOR produced oil samples.

6. REFERENCES

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APPENDIX A

TABLES

Table A1. Weight Percent Determination of Asphaltenes and Maltenes in Murphy Eyehill Oil

Sample	Date of Sampling	API Gravity at 15/15°C	N	Wt % Asphaltenes	Wt %[1] Maltenes
	May/87	12.8	4	14.4 ± 0.4	85.6 ± 0.4
1-21	January/89	13.0	8	12.5 ± 0.2	87.5 ± 0.2
	June/89	13.0	4	12.3 ± 0.1	87.7 ± 0.1
	May/87	17.3	4	10.0 ± 0.1	90.0 ± 0.1
9-16	January/89	15.7	8	10.4 ± 0.5	89.6 ± 0.5
	June/89	15.4	4	10.0 ± 0.2	90.0 ± 0.2
	May/87	N/A	4	15.1 ± 0.3	84.9 ± 0.3
16-16	Jan/89	14.2	8	12.8 ± 0.4	87.2 ± 0.4
	June/89	13.6	7	13.2 ± 0.4	86.8 ± 0.4
	May/87	N/A	4	13.3 ± 0.1	86.7 ± 0.1
D16-16	Jan/89	12.8	7	13.2 ± 0.5	86.8 ± 0.5
	June/89	12.8	8	12.7 ± 0.1	87.3 ± 0.1

[1]Maltenes are calculated by difference (i.e. weight of crude--weight of asphaltene).

N = number of runs.

Wt % Asphaltenes = Weight percent of asphaltenes in total weight of oil sample.

Wt % Maltenes = Weight percent of maltenes in total weight of oil sample.

Table A2. Weight Percent Determination of SARA Fractions in Murphy Eyehill 1-21 and 9-16 Oils Using Syncrude Method*

Sample	1-21			9-16		
	1985	May/87	June/89	1985	May/87	June/89
Saturates	19.1	22.7	33.8	23.0	16.6	37.0
Aromatics	48.1	37.1	36.3	29.4	31.7	34.7
Resins	21.1	25.3	14.6	19.1	22.1	14.4
Asphaltenes	11.5	12.0	11.7	7.5	8.7	10.9
Total Wt Recovery	99.8	97.1	96.4	79.0	79.1	97.0

*By single determination only.

Table A3. Weight Percent Determination of SARA Fractions in Murphy Eyehill 1-21, May 1987 Using HPLC and Syncrude Methods

Sample	HPLC	Syncrude
Saturates	25.1	33.8
Aromatics	45.9	36.3
Resins	13.4	14.6
Asphaltenes	14.9	11.7
Total Recovery	99.4	96.4

Table A4. Weight Percent Determination of SARA Fractions in Murphy Eyehill 9-16, May 1987 Using HPLC and Syncrude Methods

Sample	HPLC	Syncrude
Saturates	24.4	16.6
Aromatics	46.0	31.7
Resins	11.5	22.1
Asphaltenes	10.1	8.7
Total Recovery	99.0	79.1

Table A5. Weight Percent of Solvents in the Given Saturate and Aromatic Fractions of 16-16 and D16-16 of June/89

	Sample	Pentane and Methylene Chloride	Hexane
Saturates	16-16 S	1.6	0.4
	D16-16 S	0.26	0.09
Aromatics	16-16 A	2.8	0.8
	D16-16 A	0.37	0.13

Table A6. H_{Al}/H_{Ar} of the Aromatic Fractions Based on NMR Analysis

Sample	1-21	9-16	16-16	D16-16
May/87	11.98	13.92	17.86	9.52
Jan/89	11.50	15.66	9.20	19.00
June/89	11.50	12.17	31.53	18.23

Table A7. C_{Al}/C_{Ar} of the Aromatic Fractions Based on NMR Analysis

Sample	1-21	9-16	16-16	D16-16
May/87	1.41	2.00	3.25	2.01
Jan/89	2.33	2.05	2.30	2.86
June/89	1.96	1.23	1.41	2.43

Table A8. H_{Al}/H_{Ar} of the Resin Fractions Based on NMR Analysis

Sample	1-21	9-16	16-16	D16-16
May/87	12.88	23.39	24.00	32.33
Jan/89	18.60	27.57	19.00	13.28
June/89	16.54	15.39	34.71	13.49

Table A9. C_{Al}/C_{Ar} of Resin Fractions Based on NMR Analysis

Sample	1-21	9-16	16-16	D16-16
May/87	0.94	1.52	3.73	2.34
Jan/89	1.97	3.50	3.04	1.96
June/89	1.82	1.58	1.00	2.67

Table A10. Percent SAR Fractions of Murphy Eyehill 1-21 Oil (June 1989) According to NMR Analysis

	^{1}H		^{13}C	
Sample	Aromatics	Aliphatics	Aromatics	Aliphatics
HPLC				
Saturates	0	100	0	100
Aromatics	8.0	92.0	33.8	66.3
Resins	5.7	94.3	35.3	64.7
Syncrude				
Saturates	0.6	99.4	2.3	97.7
Aromatics	4.6	95.4	38.1	61.9
Resins #1	4.8	95.2	24.6	75.4
Resins #2	4.0	96.0	42.1	57.9

Table A11. Percent Fractions of Murphy Eyehill Oil 9-16 (June 1989) According to NMR Analysis

	^{1}H		^{13}C	
Sample	Aromatics	Aliphatics	Aromatics	Aliphatics
HPLC				
Saturates	0.2	99.8	0	100
Aromatics	7.6	92.5	44.8	55.2
Resins	6.1	93.9	38.7	61.3
Syncrude				
Saturates	1.7	98.3	4.7	95.3
Aromatics	6.6	93.4	40.1	59.9
Resins #1	2.2	97.8	36.3	63.7
Resins #2	1.7	98.3	32.3	67.7

Table A12. Aromatic Cross-Contamination in Saturate Fractions Obtained from Two Different Methods

Methods*	Saturates Injected (mg/mL)	Response Factor for Aromatics (Counts/mg) ($x10^9$)	Wt % Contamination
HPLC	1.93	1.430	3.03
Syncrude	46.74	0.935	10.24

*Saturates of well 1-21 of June 1989.

Table A13. Crude Oil 1-21 (June 1989) NMR Analysis

Type	Aromatics	Aliphatics	Aliph/Arom.
^{1}H	6.2	93.8	15.13
^{13}C	19.5	80.5	4.13

Table A14. Calculated NMR Signals for Oil 1-21 (June/89) from the Weighted Experimental NMR Data of the SARA Fractions

Type	Signal Assigned to SARA Fraction	NMR Signal Assigned to: Aromatics	Aliphatics
^{1}H	Saturates	-	26.5
	Aromatics	3.87	44.53
	Resins	0.78	12.82
	Asphaltenes	1.29	11.00
	Oil (Calculated)	5.94	94.85
^{13}C	Saturates	-	26.50
	Aromatics	16.36	32.09
	Resins	4.80	8.74
	Asphaltenes	5.62	6.68
	Oil (Calculated)	26.78	74.00